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(54) Process to Improve the Demulsification of Bitumen in Pond Oil

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ABSTRACT

A process for the recovery of bitumen from pond oil by breaking the aqueous pond oil emulsion with an aluminum polyhydroxy polymer having a hydrolysis ratio (OH/Al) of from about 2 to about 2.2 or a combination of said polymer with a demulsifier, allowing the treated emulsion to stand until water released from the emulsion is coalesced and separating the bitumen.

PROCESS TO IMPROVE THE DEMULSIFICATION OF BITUMEN IN POND OIL

This invention is directed to a novel method to enhance the demulsification of bitumen in pond oil, which is a waste product in the conversion of tar sands to petroleum products, and thereby enable the bitumen in the pond oil to be more efficiently recovered.

BACKGROUND OF THE INVENTION

Tar sands (which are also known as oil sands and bituminous sands) are sand deposits which are impregnated with dense, viscous petroleum. Tar sands are found throughout the world, often in the same geographical areas as conventional petroleum. The largest deposit, and the only one of present commercial importance, is in the Athabasca region in the northeast section of the province of Alberta, Canada. While much of the Athabasca deposit is not economically recoverable on a commercial scale with current technology, nonetheless, a substantial portion is situated at, or very near, the surface where it may fairly readily be mined and processed into synthetic crude oil, and this procedure is being carried out commercially on a very large scale by Great Canadian Oil Sands (now Suncor, Inc., Oil Sands Division) and by Syncrude near Fort McMurray, Alberta.

Athabasca tar sands is a three-component mixture of bitumen, minerals and water. Bitumen is the valuable component for the extraction of which tar sands are mined and processed. The bitumen content is variable, averaging 12 wt%

of the deposit, but ranging from zero to 18 wt%. Water typically runs 3 to 6 wt% of the mixture, and generally increases as the bitumen content decreases. The mineral content is relatively constant, ranging from 84 to 86 wt%.

While several basic extraction methods to separate the bitumen from the sand have been known for many years, the "hot water" process is the only one of present commercial significance and is employed by both Suncor and Syncrude. The hot water process for achieving primary extraction of bitumen from tar sand consists of three major process steps (a fourth step, final extraction, is used to clean up the recovered bitumen from downstream processing). In the first step, called conditioning, tar sand is mixed with water and heated with open steam to form a pulp of 70 to 85 wt% solids. Sodium hydroxide or other reagents are added as required to maintain pH in the range of 8.0-8.5. In the second step, called separation, the conditioned pulp is diluted further so that settling can take place. The bulk of the sand-size mineral rapidly settles and is withdrawn as sand tailings. Most of the bitumen rapidly floats (settles upwardly) to form a coherent mass known as froth which is recovered by skimming the settling vessel. A third stream, called the middlings drag stream, may be withdrawn from the settling vessel and subjected to a third processing step, scavenging, to provide incremental recovery of suspended bitumen.

The throwaway material from above extractive processing is referred to as tailings and these tailings are an aqueous

suspension of minerals (sand and other mineral fines), and bitumen and this sludge is discharged to large lagoons or ponds. Over time, the tailings sludge matures, causing the bitumen in the tailings discharged to the pond to coagulate to some extent and form an irregular layer of varying thickness suspended between the compressed higher density bottom sludge and the lower density upper aqueous layer.

It is, of course, desirable to recover the bitumen from the lagoon and if the location and thickness of the suspended bitumen is known, an appropriate pump can be used to remove it. This bitumen is recovered as an aqueous emulsion and this emulsion, referred to herein as "pond oil," is extremely stable and difficult to completely break with the commonly available demulsifiers.

This invention is directed to breaking such bitumen-containing pond oil emulsions and recovering the bitumen from the water coalesced by the process of the invention.

DISCUSSION OF THE PRIOR ART

Numerous demulsifiers are known in the prior art and although some of them do show demulsification effects with pond oil, their effectiveness is inadequate for economic bitumen recovery from pond oil. Typical of such emulsifiers are: (1) D-415 and D-416 which are blends of polymers in a mixture of a heavy aromatic solvent, xylene and isopropyl alcohol; (2) D-420 which is a polymer blend in an aromatic solvent and methanol; (3) 5E-40 which is a polyal condensate in a high boiling point alkylaromatic solvent. D-415, D-416,

and D-420 are manufactured by United Oilfield Chemicals, Ltd. of Nisku, Alberta, Canada, and 5E-40 is manufactured by Alchem, Inc. in Burlington, Ontario, Canada. The demulsifier agents D-415, D-416, and 5E-40 are soluble in aromatic solvents such as toluene. D-420, however, is a water dispersible agent. Both types of demulsifiers may, of course, be used. Because of their relatively high costs and/or low efficiency, none of these agents by themselves are totally satisfactory as demulsifiers for recovering bitumen from pond oil.

BRIEF STATEMENT OF THE INVENTION

In accord with this invention, recovery of bitumen from pond oil is enhanced by treating pond oil with an aluminum hydroxy polymer having a hydrolysis ratio of from about 2.0 to about 2.2 or with a combination of an emulsion breaking chemical and the aluminum polyhydroxy polymer wherein the ratio of hydroxyl groups to aluminum atoms (the hydrolysis ratio) is between about 2.0 and about 2.2.

More particularly, the invention comprises a process for the recovery of bitumen from an aqueous emulsion of pond oil obtained from the waste tailings lagoons of oil sands processing by treating the pond oil with an aluminum polyhydroxy polymer having a hydrolysis ratio of from about 2.0 to about 2.2 or with such polymer and a commercial demulsifier to break the emulsion, allowing the treated emulsion to stand until water from the broken emulsion is coalesced and recovering the bitumen.

DETAILED DESCRIPTION OF THE INVENTION

As indicated above, the essence of this invention lies in the use of an aluminum polyhydroxy polymer. This polymer is positively charged and is characterized by having an aluminum atom in a tetrahedral configuration, which aluminum atom is surrounded by twelve aluminum atoms in an octahedral configuration and the remaining valences of this polymer is comprised of hydroxyl groups. This inorganic polymer is quite stable up to a temperature of about 500°C. Reference to this polymer and its preparation will be found in the article by J. Y. Bottero et al entitled "Mechanism of Formation of Aluminum Trihydroxide From Keggin Al_{13} Polymers," Journal of Colloid and Interface Science, Vol. 117, No. 1, May 1987, pages 47-57.

The aluminum polyhydroxy polymer appears to have several positive effects on the pond oil emulsion. One effect is that it destabilizes the particulate clay minerals in the pond oil emulsion causing those particulates to settle as an enlarged porous volume and thereby taking the water droplets with the clay minerals. It is the escape of these water molecules that tends to effect a slight demulsification. But more significantly, a second beneficial effect is believed to be due to the positive charge on the aluminum polyhydroxy polymer. During the processing of the oil sands, the use of caustic and the oxidation which occurs over time creates surface active agents which generally have a negative charge due to the carboxyl groups on such surfactant

molecules. Such agents act to strongly emulsify the bitumen in the pond oil. The positively charged aluminum polyhydroxy polymer, however, is believed to absorb the negatively charged surfactants and thus, the demulsifiers may readily demulsify the system whereby the water present is coalesced and the bitumen released for recovery.

The aluminum polyhydroxy polymer is readily prepared just before use by reaction of sodium hydroxide with aluminum chloride or other water soluble aluminum salt. In preparing a solution of the polymer, molar amounts of these reagents are preferably used so as to give a hydrolysis ratio (i.e., a molar ratio of OH/Al) of from about 2.0 to about 2.2. Thus, for a ratio of 2.2, 1.1 mole of NaOH and 0.5 mole of aluminum chloride will be used. This ratio is important in order to achieve the proper configuration of aluminum atoms referred to above. Alternatively, the polymer may be made with a higher OH/Al ratio and the product so obtained then be diluted with an appropriate amount of alum solution so as to reduce the ratio between about 2.0 and 2.2. Thus, for example, a liquid sodium aluminate solution which has an OH/Al ratio of 5 (commercially available as HAN-FLOC 45™ from Hydro-Tech Limited, New Westminster, British Columbia and is a trademark of Handy Chemicals of Montreal) may be diluted with an aluminum chloride or alum solution to the desired ratio.

In carrying out the process of the invention, an aqueous solution of the aluminum hydroxy polymer is added to the pond oil with or without the commercial demulsifier and, after

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mixing, much of the water from the broken emulsion is coalesced. The bitumen is then readily recovered by centrifuging or other means and taken for further processing.

As indicated, the aluminum polyhydroxy polymer may be used alone, but its performance will vary to some extent with the particular source of pond oil. In those instance where the effect of the polymer is of limited performance, it is desirable to use the polymer in combination with commercial demulsifiers to get an additive effect. Since the aluminum polymer is less costly than the emulsifiers used, the combination results in a more efficient process at less cost than use of high concentrations of emulsifiers alone. The demulsifying amounts of materials used are not critical, but in general, both the commercial emulsifier and aluminum polymer will be used in an amount of from about 25 to about 100 parts per million (ppm) of pond oil. It will be understood that in order to obtain optimum economics and performance, the preferred amounts of each agent will be determined by experiment.

In order to further exemplify the invention, the following examples are given.

Experimental Procedures

Preparation of Aluminum Polyhydroxy Polymer

A solution of the aluminum polyhydroxy polymer was prepared by the addition of an aqueous solution of 1.1 M NaOH to a stirred 0.5 M aqueous aluminum chloride solution at a rate of about 3 ml./min. and at a temperature of about

20°C. The hydrolysis ratio (OH/Al) of the resulting inorganic polymer was 2.2.

Demulsifiers Evaluated

Commercially available demulsifiers were used in the evaluations and these were D-416, D-420, and 5R-40 referred to above.

Pond Oil Sample

The pond oil used in the evaluation was taken from a commercial tailings pond at the Suncor, Inc. oil sands processing plant at Fort McMurray, Alberta. This material contained visible free water which was removed and the sample then subjected to analysis as follows:

	W/W%
Bitumen	50.6
Minerals	1.4
Water	41.3
Light Hydrocarbons	6.7

During the processing of the oil sands a hydrocarbon diluent is added to the recovered bitumen froth in order to facilitate a centrifugation step. Some of this diluent ultimately accumulates in the pond oil and in order to maintain a consistent standard for the experimental evaluations the ratio of diluent to bitumen in the pond oil (from which the free water has been removed) is adjusted with toluene to a ratio of 0.6.

Experimental Demulsification Procedure

A 78 ml. sample of the pond oil with appropriate amounts

of aluminum hydroxy polymer alone or with a demulsifier was placed in a 100 ml. capacity centrifuge tube and 22 ml. of toluene added to reduce the viscosity. The contents of the centrifuge tube were thoroughly mixed and held in a hot water bath at 82°C. for 10 minutes. The heated test sample was then centrifuged at 2000 r.p.m. for 10 minutes whereby the contents of the tube were separated into a small bottom sediment layer of silt and clays, a moderate middle layer of water and a large upper layer of bitumen which contained some water.

The bitumen layer was then separated off and subjected to water analysis by the Dean Stark method.

Experimental Results

The tables which follow show the effectiveness of the use of the aluminum polyhydroxy polymer in conjunction with commercial demulsifiers. The lower the amount of water in the recovered bitumen, the greater the effectiveness of the treatment. The term "polymer" used in the tables refers to the aluminum polyhydroxy polymer. It will be observed that the aluminum polyhydroxy polymer alone is effective in reducing the amount of water in the recovered bitumen and the emulsifier alone also shows some effect. However, by use of both of the agents and when the polymer is used at appropriate concentrations, the water reducing effect is most pronounced. The percent improvement due to the polymer alone as shown in the tables is calculated by dividing the difference between the values for percent water where no

demulsifier is used and the control value of each table by the control value and multiplying by 100. The total percent improvement reflects the performance due to the aluminum polymer in combination with the demulsifier and and is calculated by dividing the difference between the values for percent water where both the aluminum polymer and demulsifier are used by the control value and multiplying by 100.

As can be seen from the tables which follow, the use of aluminum polyhydroxy polymer alone or in combination with the commercial demulsifiers is quite beneficial in dewatering (e.g., demulsification) of the pond oil. In the examples given the percent improvement for use of the aluminum polymer alone ranges from about 1.5% to about 41%. Even the lower value of 1.5% is a very significant benefit because of the very large volumes of pond oil processed for recovery of bitumen. It is also evident from the data that the use of aluminum polymer in combination with commercial demulsifier significantly increases the recovery of bitumen from pond oil over use of the demulsifier alone.

Table 1

Percent Water Remaining in Bitumen Layer after Treatment with Polymer and D-416

D-416 (ppm)	Polymer (ml./100 ml. sample) 0.0	0.25	0.75	1.0
0.0	20.2*	19.9	19.3	16.4
25	15.7	15.4	14.6	13.9
50	13.4	13.2	12.7	11.9
100	12.9	12.9	12.7	12.1

*Control Value

Percent Improvement

D-416 (ppm)	Polymer Concentration (ml./100 ml.) 0.0	0.25	0.75	1.0
0.0				
Due to polymer alone	---	1.49	4.46	18.81
25				
Due to polymer alone	---	1.91	7.01	11.46
Total % Improvement	22.39+	23.88	27.86	31.34
50				
Due to polymer alone	---	1.49	5.22	11.19
Total % Improvement	33.66+	34.65	37.13	41.09
100				
Due to polymer alone	---	0.00	1.55	6.20
Total % Improvement	36.14+	36.14	37.13	40.10

+Improvement due only to demulsifier

Table 2

Percent Water Remaining in Bitumen Layer after Treatment with Polymer and 5E-40

	Polymer (ml./100 ml. sample)		
5E-40 (ppm)	0.0	0.5	1.0
0.0	22.8*	19.6	16.6
50	19.2	16.0	15.7
100	18.9	14.2	13.8

*Control value

Percent Improvement

	Polymer Concentration (ml./100 ml.)		
5E-40 (ppm)	0.0	0.25	1.0
0.0			
Due to polymer alone	---	14.04	27.19
50			
Due to polymer alone	---	16.67	18.23
Total % Improved	15.79+	29.82	31.14
100			
Due to polymer alone	---	24.87	26.98
Total % Improved	17.11+	37.72	39.47

+Improvement due only to demulsifier

Table 3

Percent Water Remaining in Bitumen Layer after Treatment with Polymer and D-420

D-420 (ppm)	Polymer (ml./100 ml. sample) 0.0	0.5	1.0
0.0	23.3*	---	21.7
50	21.2	19.4	17.4
100	19.2	19.1	16.8

*Control value

Percent Improvement

D-420 (ppm)	Polymer Concentration (ml./100 ml.) 0.0	50	100
0.0			
Due to polymer alone	---	---	21.70
50			
Due to polymer alone	---	8.49	17.92
Total % Improved	9.01+	16.74	25.32
100			
Due to polymer alone	---	0.52	12.50
Total % Improved	17.60+	18.03	27.90

+Improvement due only to demulsifier

CLAIMS

1. A process for the recovery of bitumen from an aqueous emulsion of pond oil obtained from the waste tailings lagoons of oil sands processing which comprises treating said pond with a demulsifying amount of aluminum polyhydroxy polymer wherein the hydroxyl to aluminum ratio is between about 2.0 and about 2.2 to break said emulsion, allowing the treated emulsion to stand until water from said broken emulsion is coalesced and recovering said bitumen.

2. The process of Claim 1 wherein the amount of said aluminum polymer used is from about 25 to about 100 ppm of pond oil.

3. A process for the recovery of bitumen from an aqueous emulsion of pond oil obtained from the waste tailings lagoons of oil sands processing which comprises treating said pond oil emulsion with a commercial demulsifier and an aluminum polyhydroxy polymer wherein the hydroxyl to aluminum ratio is between about 2.0 and about 2.2 to break said emulsion, allowing the treated pond oil to stand until water from said broken emulsion is coalesced and recovering said bitumen.

4. The process of Claim 3 wherein the demulsifier and the aluminum polyhydroxy polymer is each used in an amount from about 25 to about 100 ppm of pond oil.

5. The process of Claim 4 wherein the demulsifier is soluble in an aromatic solvent.

6. The process of Claim 4 wherein the demulsifier is water dispersible.

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente